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COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the
Transport of Dangerous Goods
(Fourteenth session,
Geneva, 8-18 December 1997,
agenda item 2 (d))

DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Other draft amendments

Damaged packagings

Transmitted by the Expert from the United Kingdom

Justification

In 1994 the International Air Transport Association (IATA) reported that a number of packages, some containing dangerous goods, had been found to be leaking on aircraft, mainly in Europe. During the Sub-Committee session in July 1994, a special working group was convened but no proposals to change the Recommendations were made at that time. During the last 3 years several further incidents have been reported and the Civil Aviation Authority in the United Kingdom arranged for some tests to be undertaken to try to identify a common cause of the problem, mainly damage to the chimbs of metal drums.

There would appear to be two causes. Firstly, consignors are not considering sufficiently the hazards that a package might encounter during transport e.g. manual handling and transhipment. Secondly maintenance of certain narrow-bodied aircraft holds, notably loose hardened metal screws in the floors together with a dragging method of loading individual drums, may be responsible for some damage. It seems that although UN packagings have been used, consignors fail to take full account of the conditions that may be encountered in transport, particularly on a long journey that may involve carriage on more than one means of transport thus increasing the potential for damage through additional loading/unloading.

More recently there have been reports of similar damage occurring in freight containers and on road vehicles. A recent letter to Hazardous Cargo Bulletin from New Zealand confirmed that this was not simply a European problem.

The expert from the United Kingdom therefore proposes that the text in the Packing Provisions in Part 4 and the Provisions Concerning Transport Operations in Part 7 are clarified and augmented to require both consignors and operators to take account of conditions likely to be encountered in transport.

Proposal

1. Amend paragraph 4.1.1.1 to read as follows:

4.1.1.1 Dangerous goods shall be packed in packagings (new, reconditioned or reused) of good quality. Packagings shall be strong enough to withstand the shocks and loadings normally encountered during transport, including trans-shipment between transport units and/or warehouses as well as any removal from a pallet or overpack for subsequent manual handling. Packagings shall be constructed and closed so as to prevent any leakage from the package as prepared for transport which might be caused under normal conditions of transport, by vibration, or by changes in temperature, humidity or pressure (resulting from altitude, for example). No harmful quantity of dangerous residue shall adhere to the outside of packages.

2 Add the following two new paragraphs to Chapter 7.1:

7.1.1.3 Dangerous goods shall be secured in the transport unit in a manner that will prevent any movement during the journey which would change the orientation of the package or cause it to be damaged.

7.1.1.4 During loading dangerous goods shall be protected from being damaged. Particular attention shall be paid to the handling of packages during their preparation for transport to the type of transport unit on which they are to be carried and to the method of loading, so that accidental damage is not caused through dragging or mishandling of the packages.

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**Sub-Committee of Experts on the
Transport of Dangerous Goods
(Fourteenth session,
Geneva, 8-18 December 1997,
agenda item 2 (b))**

DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Use of packagings and IBCs

Chapter 4.1

Transmitted by the Expert from the United Kingdom

Justification

1. Editorial Revision of Chapter 4.1

In the 10th Edition of the Recommendations a number of paragraphs were moved from Chapter 9 and Chapter 16 into Chapter 4.1. During a review of the new text, duplication of certain provisions for packagings and IBCs was recognised. At its Thirteenth Session in July 1997, the Sub-Committee adopted new provisions for large packagings (ST/SG/AC.10/ C.3/1997/35/Rev.1). The resulting further amendments to Chapter 4.1 would have increased this duplicated text.

This duplication is unnecessary and confusing. Packagings, IBCs and large packagings should be used under the same general provisions.

"Note 2" under the examples would be deleted and Notes 3 and 4 renumbered. The table was taken from the ICAO Technical Instructions. Note 2 is incomplete but in fact only deals with specific conditions for air transport. It is not intended to include this Note in Amendment 30-98 to the IMDG Code.

The Expert from the United Kingdom therefore proposes an editorial revision to Chapter 4.1.1 to combine the common text.

2. Consequential Changes

1. 4.1.1.14 requires packagings to be manufactured under a quality assurance programme. The equivalent provision for IBCs will be found in 6.5.1.6.1 and that for large packagings is in 6.6.1.2. As quality assurance is not a packaging user responsibility and to align with the other chapters, it is proposed to move 4.1.1.14 to 6.1.1.4.

2. There are cross references in 6.5 which need to be altered to reflect the new style.

Proposal

Chapter 4.1 Use of Packagings, Intermediate Bulk Containers (IBCs) and Large Packagings

Note 1: ***Packing groups***

Dangerous goods of all classes other than Classes 1, 2, and 7 and divisions 5.2 and 6.2 have for packing purposes been divided among three groups according to the degree of danger they present, i.e.

Substances presenting	*high danger*	*Packing Group I;*
Substances presenting	*medium danger*	*Packing Group II; and*
Substances presenting	*low danger*	*Packing Group III.*

[to align with 2.0.1.3]

The packing group to which a substance is assigned is indicated in the Dangerous Goods List in Chapter 3.2.

Note 2: ***Explosives, self-reactive substances and organic perioxides***

Unless specific provision to the contrary is made in these Regulations, the packagings, IBCs or large packagings used for goods of Class 1, self-reactive substances of Division 4.1 and organic peroxides of Division 5.2 shall comply with the provisions for the medium danger group (Packing Group II).

4.1.1 **General provisions for the packing of dangerous goods, other than goods of Classes 2 or 7 or Division 6.2, in packagings, IBCs or large packagings.**

4.1.1.1 Dangerous goods shall be packed in packagings, IBCs or large packagings of good quality. They shall be constructed and provided with closure devices so as to prevent any loss of contents from the package as prepared for transport which might be caused under normal conditions of transport, by vibration, or by changes in temperature, humidity or pressure (resulting from altitude, for example). No dangerous residue shall adhere to the outside of packages, IBCs or large packagings during transport. These provisions apply to new, reused, reconditioned or remanufactured packagings, IBCs or large packagings, as appropriate.

[i.e include 4.1.2.4]

4.1.1.2 Parts of packagings, IBCs or large packagings which are in direct contact with dangerous goods

(a) shall not be affected or significantly weakened by those dangerous goods.

(b) shall not cause a dangerous effect in the package e.g. catalysing a reaction or reacting with the dangerous goods.

Where necessary, they shall be provided with a suitable inner coating or treatment.

4.1.1.3 Unless provided elsewhere in these Regulations, each packaging, except inner packagings of combination packagings, IBC or large packagings, shall conform to a design type successfully tested in accordance with the requirements laid down in 6.1.5, 6.5.4 or 6.6.5.

4.1.1.4 When filling packagings, IBCs or large packagings with liquids, sufficient ullage (outage) shall be left to ensure that neither leakage nor permanent distortion of the packaging occurs as a result of an expansion of the liquid caused by temperatures likely to occur during transport. Unless specific requirements are prescribed in national or international rules, agreements or recommendations, liquids shall not completely fill a packaging at a temperature of 55 °C. Sufficient ullage shall be left in an IBC to ensure that at the mean bulk temperature of 50°C it is not filled to more than 98% of its water capacity.

[i.e. include 4.1.2.2.]

4.1.1.4.1 For air transport, packagings intended to contain liquids shall also be capable of withstanding a pressure differential without leakage as specified in the international regulations for air transport.

4.1.1.5 Inner packagings shall be packed in an outer packaging in such a way that, under normal conditions of transport, they cannot break, be punctured or leak their contents into the outer packaging. Inner packagings that are liable to break or be punctured easily, such as those made of glass, porcelain or stoneware or of certain plastics materials, etc., shall be secured in outer packagings with suitable cushioning material. Any leakage of the contents shall not substantially impair the protective properties of the cushioning material or of the outer packaging.

4.1.1.6 Dangerous goods shall not be packed together in the same outer packaging with dangerous or other goods if they react dangerously with each other and cause:

(a) combustion and/or evolution of considerable heat;

(b) evolution of flammable, toxic or asphyxiant gases;

(c) the formation of corrosive substances; or

(d) the formation of unstable substances.

4.1.1.7 The closures of packagings containing wetted or diluted substances shall be such that the percentage of liquid (water, solvent or phlegmatizer) does not fall below the prescribed limits during transport. Where two or more closure systems are fitted in series on an IBC, that nearest to the substance being carried shall be closed first.

[i.e include 4.1.2.3]

4.1.1.8 1/ Where pressure may develop in a package by the emission of gas from the contents (as a result of temperature increase or other cause), the packaging may be fitted with a vent, provided that the gas emitted will not cause danger on account of its toxicity, its flammability, the quantity released, etc. The vent shall be so designed that, when the packaging is in the attitude in which it is intended to be transported, leakages of liquid and the penetration of foreign matter are prevented under normal conditions of transport. Venting of the package is not permitted for air transport.

4.1.1.9 New, remanufactured, reused packagings, IBCs or large packagings or reconditioned packagings or repaired IBCs shall be capable of passing the tests prescribed in 6.1.5, 6.5.4 or 6.6.5. Before being filled and handed over for transport, every packaging, IBC or large packaging shall be inspected to ensure that it is free from corrosion, contamination or other damage and with regard to proper functioning of any IBC service equipment. Any packaging, IBC or large packaging which shows signs of reduced strength as compared with the approved design type shall no longer be used or shall be so reconditioned, or repaired, that it is able to withstand the design type tests.

[i.e. include 4.1.2.1].

4.1.1.10 Liquids shall be filled only into packagings or rigid plastics IBCs or composite IBCs with inner plastics receptacles, which have an appropriate resistance to the internal pressure that may develop under normal conditions of transport. Packagings or such IBCs marked with the hydraulic test pressure prescribed in 6.1.3.1(d) or 6.5.2.2.1 shall be filled only with a liquid having a vapour pressure:

1/ [Note: New first sentence added at the Sub-Committee (see -/CRP2/Add.5) is unnecessary as it is already covered in 4.1.1.10]

(a) such that the total gauge pressure in the packaging (i.e. the vapour pressure of the filling substance plus the partial pressure of air or other inert gases, less 100 kPa) at 55°C, determined on the basis of a maximum degree of filling in accordance with 4.1.1.4 and a filling temperature of 15°C, will not exceed two thirds of the marked test pressure; or

(b) at 50 °C less than four sevenths of the sum of the marked test pressure plus 100 kPa, or

(c) at 55 °C less than two thirds of the sum of the marked test pressure plus 100 kPa.

[i.e. include 4.1.2.11.2]

EXAMPLES OF REQUIRED MARKED TEST PRESSURES FOR PACKAGINGS CALCULATED AS IN 4.1.1.10 (c)

UN No.	Name	Class	Packing Group	V_{p55} (kPa)	V_{p55} x 1.5 (kPa)	(V_{p55} x 1.5) minus 100 (kPa)	Required minimum test pressure gauge under 6.1.5.5.4(c) (kPa)	Minimum test pressure (geuge) to be marked on the packaging (kPa)
2056	Tetrahydrofuran	3	II	70	105	5	100	100
2247	n-Decane	3	III	1.4	2.1	-97.9	100	100
1593	Dichloromethane	6.1	III	164	246	146	146	150
1155	Diethyl ether	3	I	100	299	199	199	250

Note 1: *For pure liquids the vapour pressure at 55 °C (V_{p55}) can often be obtained from scientific tables.*

Note 2: *The table refers to the use of 4.1.1.10 (c) only, which means that the marked test pressure shall exceed 1.5 times the vapour pressure at 55 °C less 100 kPa. When, for example, the test pressure for n-decane is determined according to 6.1.5.5.4 (a), the minimum marked test pressure may be lower.*

Note 3: *For diethyl ether the required minimum test pressure under 6.1.5.5.5 is 250 kPa.*

4.1.1.11 An empty packaging, IBC or large packaging that has contained a dangerous substance shall be treated in the same manner as is required by these Regulations for a filled packaging, IBC or large packaging unless adequate measures have been taken to nullify any hazard.

[i.e. include 4.1.2.6]

4.1.1.12 2/ Every packaging or IBC intended to contain liquids shall successfully undergo a suitable leakproofness test, and be capable of meeting the appropriate test level indicated in 6.1.5.4.3, or 6.5.4.7 for the various types of IBCs:

(a) before it is first used for transport;

(b) after remanufacturing or reconditioning of any packaging, before it is re-used for transport;

(c) after the repair of any IBC, before it is re-used for transport.

For this test the packaging or IBC need not have its closures fitted. The inner receptacle of a composite packaging, or IBC may be tested without the outer packaging, provided the test results are not affected. This test is not necessary for inner packagings of combination packagings.

[i.e. include 4.1.2.9].

4.1.1.13 Packagings, IBCs or large packagings used for solids which may become liquid at temperatures likely to be encountered during transport shall also be capable of containing the substance in the liquid state.

[i.e include 4.1.2.8]

[4.1.1.14 3/ Packagings shall be manufactured and tested under a quality assurance programme which satisfies the competent authority in order to ensure that each manufactured packaging meets the requirements of this Chapter.]

2/ Although this provision was adopted for large packagings it is in fact incorrect as there is no lead test for them in the new 6.6. 4.1.1.12 is only intended for single packagings. Large packagings are part of combination packagings.

3/ Move to a new 6.1.1.4 for packagings and 6.6.1.2 for large packagings since quality assurance concerns the manufacturer before the user and the equivalent for IBCs is already in 6.5.1.6.1. [Already noted for the reformatted IMDG Code.]

4.1.1.15 4/ During transport, IBCs and large packagings shall be securely fixed or packed into the transport unit so as to prevent lateral or longitudinal movement or impact and so as to provide adequate external support.

[i.e. include 4.1.2.5]

4.1.1.16 5/ *Use of salvage packagings*

4.1.1.16.1 Damaged, defective or leaking packages, or dangerous goods that have spilled or leaked may be transported in salvage packagings prescribed in 6.1.5.1.11. This does not prevent the use of larger size packagings of appropriate type and performance level under the conditions of 4.1.1.16.2.

4.1.1.16.2 Appropriate measures shall be taken to prevent excessive movement of the damaged or leaking packages within a salvage packaging. When the salvage packaging contains liquids, sufficient inert absorbent material shall be added to eliminate the presence of free liquid.

4.1.2 **Additional general provisions for the use of IBCs**

4.1.2.1 to 4.1.1.9

4.1.2.2 to 4.1.1.4

4.1.2.3 to 4.1.1.7

4.1.2.4 to 4.1.1.1

4.1.2.5 to 4.1.1.15 (or 7.1.1.X)

4.1.2.6 to 4.1.1.11

4.1.2.1 When IBCs are used for the transport of liquids, with a flash point of 60.5°C (closed cup) or lower, or of powders liable to dust explosion, measures shall be taken to prevent a dangerous electrostatic discharge.

[Formerly 4.1.2.7]

4.1.2.8 to 4.1.1.13

4/ Note: This paragraph should be moved to a new paragraph 7.1.1.X. In -/CRP2/Add.5 the Secretary proposes that this paragraph is moved to Part 7.

5/ [Note: If 4.1.1.14 is moved to 6.1.1.4 and 4.1.1.15 is moved to 7.1.1.X existing 4.1.1.16 becomes 4.1.1.14].

4.1.2.9 to 4.1.1.12

4.1.2.2 The periodic testing and inspection requirements for IBCs are provided in Chapter 6.5. An IBC shall not be filled and offered for transport after the date of expiry of the last periodic test required by 6.5.4.14.3, or the date of expiry of the last periodic inspection required by 6.5.1.6.4. However, an IBC filled prior to the date of expiry of the last periodic test or inspection may be transported for a period not to exceed three months beyond the date of expiry of the last periodic test or inspection. In addition, an IBC may be transported after the date of expiry of the last periodic test or inspection:

(a) after emptying but before cleaning, for purposes of performing the required test or inspection prior to refilling; and

(b) unless otherwise approved by the competent authority, for a period not to exceed six months beyond the date of expiry of the last periodic test or inspection in order to allow the return of dangerous goods or residues for proper disposal or recycling. Reference to this exemption shall be entered in the transport document.

[Formerly 4.1.2.10]

Delete sub-heading "4.1.2.11 Additional general provisions for the use of rigid plastics and composite IBCs for liquids".

4.1.2.3 For rigid plastics IBCs and composite IBCs with plastics inner receptacles, unless otherwise approved by the competent authority, the period of use permitted for the transport of dangerous liquids shall be five years from the date of manufacture of the receptacle except where a shorter period of use is prescribed because of the nature of the liquid to be transported.

[Formerly 4.1.2.11.1]

4.1.2.11.2 to 4.1.1.10

4.1.2.4 IBCs of type 31HZ2 shall be filled to at least 80% of the volume of the outer casing and always be carried in closed transport units.

[Formerly 4.1.2.11.3 and 4.1.2.11.4].

Consequentials

6.5.3.1.7 refers to 4.1.3.2 - Should be 4.1.1.4

6.5.4.8.4.2 refers to 4.1.2.2. - Should be 4.1.1.4

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DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Other draft amendments

Additional screening procedures

Transmitted by the European Chemical Industry Council (CEFIC)

Introduction

1 It is common practice in classification that full classification tests are not performed on all the substances which are candidates for classification. Technical decisions are made on the need for particular test programmes on the basis of the physical and chemical nature of the substance, together with supplementary information from small scale screening tests. CEFIC considers that provision of example screening procedures has considerable benefits since:

- smaller quantities of materials are required for testing reducing hazards to the test personnel and impact on the environment;
- it avoids unnecessary testing with consequent reduction in costs; and
- by providing consensus example procedures, a benchmark is given.

Accordingly, CEFIC submitted draft amendments to the Manual of Tests and Criteria on additional screening procedures (see document ST/SG/AC.10/C.3/1997/4) for consideration at the 13 th session of the Sub-committee.

2. The report of the Sub-Committee of experts on its thirteenth session recognizes that it is helpful to publish a voluntary guideline on screening procedures as an appendix to the Manual of Tests and Criteria:

> "The proposal to include additional screening procedures in the Manual of Tests and Criteria to enable an adequate hazard evaluation to be carried out without the need for larger scale classification tests was widely supported in principle. The representative of CEFIC was invited to collect detailed comments from all interested delegations and to submit a revised proposal for the next session which would take account of all these comments." [paragraph 112]

3. CEFIC considered all handed in comments. Comments that helped clarifying the screening procedures were gratefully accepted. Some comments stressed the responsibility of the test authority. This was taken into account by adding a reference to paragraph 1.1.2 of the general introduction in section 1 of the Manual on Tests and Criteria in the proposed text.

One comment received concerned screening procedures for mixtures which may be flammable liquids (calculation of flash point). This comment has been taken into account by clarifying the criteria under which the procedure can be used.

Proposals

4. CEFIC proposes screening procedures for:

(a) Substances which may have explosive properties (Class 1);

(b) Mixtures which may be flammable liquids (Class 3);

(c) Substances which may be flammable solids (Class 4);

(d) Substances which may be oxidizing substances and organic peroxides (Class 5).

5. Proposed text for a new Appendix 6 to the Manual of Tests and Criteria is given in the annex to this document together with consequential amendments.

Annex

PROPOSED AMENDMENTS TO THE MANUAL OF TESTS AND CRITERIA (ST/SG/AC.10/11.REV.2)

GENERAL TABLE OF CONTENTS

Appendices *Insert a new entry to read:*

"Appendix 6 SCREENING PROCEDURES"

GENERAL INTRODUCTION

1.1.2 *Append a new sentence to read:*

"In some cases, a small scale screening procedure may be used to decide whether or not it is necessary to perform larger scale classification tests. Suitable examples of procedures are given in the introductions to some test series and in Appendix 6."

1.2.1 *Amend the last sentence to read:*

"... Test Details, on an example method for emergency relief vent sizing of portable tanks for the transport of organic peroxides and on screening procedures."

INTRODUCTION TO PART II

20.3.3.3 *Amend the last indent and append a new sentence to read:*

"using rapid heating rates (differential scanning calorimetry, heating rates should normally be in the range 2 to 5 K/min.)

If differential scanning calorimetry is used, the extrapolated onset temperature is defined as being the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak with the extrapolated baseline."

CONTENTS OF APPENDICES

Insert a new entry to read:

"6 SCREENING PROCEDURES"

NEW APPENDIX 6

Insert a new Appendix 6 to read:

APPENDIX 6

SCREENING PROCEDURES

1. Purpose

1.1 Industry uses screening procedures to identify the hazard potential of raw materials, reactive mixtures and intermediates, products and by-products. The use of such procedures is essential to ensure safety during research and development and to ensure that new products and processes are as safe as possible. These procedures usually consist of a combination of a theoretical appraisal and small-scale tests and, in many cases, enable an adequate hazard evaluation to be carried out without the need for larger scale classification tests. This reduces the quantity of material required, lessens any detrimental effect on the environment and minimizes the amount of unnecessary testing.

1.2 The purpose of this appendix is to present example screening procedures. It should be used in conjunction with any screening procedures given in the introductions to the relevant test series. With the specified safety margin, the results from the screening procedures adequately predict when it is not necessary to perform the classification test as a negative result would be obtained. They are presented for guidance and their use is not compulsory. Other screening procedures may be used provided that adequate correlation has been obtained with the classification tests on a representative range of substances and there is a suitable safety margin.

2. Scope

2.1 A hazard evaluation for a new substance should be undertaken before it is offered for transport. Initially this evaluation can use the screening procedures given in this Appendix. If the screening procedure indicates that there is a hazard, the full classification procedure should be applied.

2.2 The screening procedures are only applicable to substances and stable, homogeneous mixtures of substances. If a mixture can separate out during transport, the screening procedure should also be performed on each reactive component of the mixture in addition to the mixture.

2.3 The remarks 1.1.2 from section 1 „general introduction" are emphasized that competence on the part of the testing authority is assumed and responsibility for classification is left with them.

3. Screening procedures for substances which may have explosive properties (Class 1)

3.1 The screening procedure may be used for new substances which are suspected of having explosive properties. When considering the explosive properties of self-reactive substances of Division 4.1 or organic peroxides of Division 5.2, refer to Part II of this manual and section 5.1 of this appendix. It should not be used for substances manufactured with the intention of producing a practical explosive or pyrotechnic effect.

3.2 Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure. The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release. If the screening procedure identifies the material to be a potential explosive, the Class 1 Acceptance Procedure (see 10.3) should be applied.

Note: Neither a Series 1 type (a) propagation of detonation test nor a Series 2 type (a) test of sensitivity to detonative shock is required if the exothermic decomposition energy of organic materials is less than 800 J/g.

3.3 The acceptance procedure for Class 1 explosives need not be applied:

(a) When there are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1

Table A6.1 EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

or

(b) When the substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200.

The oxygen balance is calculated for the chemical reaction:

$$C_xH_yO_z + [x + (y/4)-(z/2)]. O_2 \circledR x. CO_2 + (y/2). H_2O$$

using the formula:

$$\text{oxygen balance} = -1600.[2.x +(y/2) -z]/\text{molecular weight}$$

or

(c) When the organic substance or a homogenous mixture of organic substances contain chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 °C. (The temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500 °C to release more than 500 J/g.) The exothermic decomposition energy may be determined using a suitable calorimetric technique (see 20.3.3.3).

or

(d) For mixtures of inorganic oxidizing substances of Division 5.1 with organic material(s), the concentration of the inorganic oxidizing substance is:

less than 15 %, by mass, if assigned to Packing Group I (high hazard) or II (medium hazard),
less than 30 %, by mass, if assigned to Packing Group III (low hazard).

3.4 When the substance is a mixture containing any known explosives, the class 1 acceptance procedure should be applied.

4. Screening procedures for mixtures which may be flammable liquids (Class 3)

4.1 The procedure only applies to possible flammable mixtures containing known flammable liquids in defined concentrations although it may contain non-volatile components e.g. polymers, additives etc. The flash point of these mixtures need not be determined experimentally if the calculated flash point of the mixture, using the method given in 4.2, is at least 5 °C greater than the relevant classification criterion and provided that:

(a) The composition of the mixture is accurately known (if the material has a specified range of composition the composition with the lowest calculated flash point should be selected for assessment);

(b) The flash point (closed cup as given in 2.3.3 of the Recommendations) of each component is known (an appropriate correlation has to be applied when these data are extrapolated to other temperatures than test conditions);

(c) The activity coefficient is known for each component as present in the mixture including the temperature dependence;

(d) The liquid phase is homogeneous.

4.2 A suitable method is described by Gmehling and Rasmussen (Ind. Eng. Chem. Fundament, **21**, 186, (1982)). For a mixture containing non-volatile components, e.g. polymers or additives, the flash point is calculated from the volatile components. It is considered that a non-volatile component only slightly decreases the partial pressure of the solvents and the calculated flash point is only slightly below the measured value.

5. Screening procedures for substances which may be flammable solids (Class 4)

5.1 *Substances which may be self-reactive substances (Division 4.1)*

The classification procedures (see section 20.4) for self-reactive substances need not be applied if:

(a) There are no chemical groups present in the molecule associated with explosive or self-heating properties; examples of such groups are given in Tables A6.1 and A6.2.

Table A6.2 EXAMPLES OF CHEMICAL GROUPS INDICATING SELF-REACTIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
Mutually reactive groups	Aminonitriles, haloanilines, organic salts of oxidizing acids
S=O	Sulphonyl halides, sulphonyl cyanides, sulphonyl hydrazides
P-O	Phosphites
Strained rings	Epoxides, aziridines
Unsaturation	Olefins, cyanates

or

(b) For a single organic substance or a homogeneous mixture of organic substances, the onset of exothermic decomposition is greater than 175 °C or the exothermic decomposition energy is less than 300 J/g. The onset temperature and isothermal decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3).

5.2 *Substances which may be liable to spontaneous combustion (Division 4.2)*

5.2.1 The classification procedure for *pyrophoric solids and liquids* need not be applied when experience, in production or handling, shows that the substance do not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

5.2.2 The classification procedure for *self-heating substances* need not be applied if the results of a screening test can be adequately correlated with the classification test and an appropriate safety margin is applied. Examples of screening tests are:

(a) The Grewer Oven test (VDI guideline 2263, part 1, 1990, *Test methods for the Determination of the Safety Characteristics of Dusts*) with an onset temperature 80 K above the reference temperature for a volume of 1 *l* (33.3.1.6).

(b) The Bulk Powder Screening Test (Gibson, N. Harper, D. J. Rogers, R. *Evaluation of the fire and explosion risks in drying powders*, Plant Operations Progress, **4** (3), 181 - 189, 1985) with an onset temperature 60 K above the reference temperature for a volume of 1 l (33.3.1.6).

5.3 *Substances which in contact with water may react to emit flammable gases (Division 4.3)*

The classification procedure for substances which may react with water to emit flammable gases need not be applied if:

(a) The chemical structure of the substance does not contain metals or metalloids; or

(b) Experience in production or handling shows that the substance does not react with water, e.g. the substance is manufactured in water or washed with water; or

(c) The substance is known to be soluble in water to form a stable mixture.

6. Screening procedures for substances which may be oxidizing substances and organic peroxides (Class 5)

6.1 *Substances which may be oxidizing substances (Division 5.1)*

6.1.1 For *organic compounds*, the classification procedure for oxidizing substances of Division 5.1 need not be applied if:

(a) The compound does not contain oxygen, fluorine or chlorine; or

(b) The compound contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

6.1.2 For *inorganic substances*, the test procedure in Section 34 need not be applied if the substance does not contain any oxygen or halogen atoms.

6.2 *Substances which may be organic peroxides (division 5.2)*

6.2.1 Organic peroxides are classified by definition based on their chemical structure and on the available oxygen and hydrogen peroxide content of formulations (see 20.2.2).

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**Sub-Committee of Experts on the
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agenda item 4 (b))**

GLOBAL HARMONISATION OF SYSTEMS OF CLASSIFICATION AND LABELLING OF CHEMICALS

Physical hazards

Joint ILO/UN Working Group on Harmonised Classification Criteria for Flammability and Reactivity

Testing Conditions for Solids

Transmitted by the Expert from the United Kingdom

Background

1. Discussions on the global harmonisation of classification and labelling systems (GHS) have highlighted that for some end points the physical condition of a substance may affect the classification. This is particularly relevant for solid materials where differences in particle size are likely to influence the test results. Some discussion of the subject has taken place, particularly in relation to solid oxidisers, but there is the need to address the issue for all end points as a matter of principle. In paper ST/SG/AC.10/C.3/1997/28 the Chairman of the working group raised this issue under "Testing Conditions for Solids", and proposed some useful ideas for discussion. This paper is intended to build on that document and proposes how the problem may be resolved in principle.

2. A fundamental concept of the GHS is that classification should be based on the intrinsic properties of substances. For solids, however, this concept is not helpful. Classification is determined relative to a standard which may be either a defined reference material or an absolute value. It is well recognised that for a specific solid chemical substance, the results obtained from a test may vary with the physical form of the material. Examples of factors known to affect test behaviour are particle size, crystal form and density. The resulting assignment into a hazard category can range from low to high danger, or the classification may change completely. A change in the physical form of a substance may leave the material either unclassified or assigned to a different hazard category.

3. Therefore, it may not be possible to have a single classification for specific solid substances. A solid may have a number of classifications depending upon certain critical parameters, and these will vary from substance to substance.

Current position

4. In the context of the intrinsic properties of a chemical substance, the idea of multiple classifications may be considered contentious, but it is already used in practice. For example, within the EU supply system (67/548/EEC) a number of metals are only classified when in powder form (e.g. alumimium powder (pyrophoric) EEC No 013-001-00-6 and aluminium powder (stabilised) EEC No 013-002-00-1 are both highly flammable). It is also reflected in general terms within the UN Recommendations, where special provision 185 or 223 can be applied; application of these special provisions often reflects the variability of behaviour in classification tests with changes in physical form. Specific multiple classifications in the transport list in Chapter 2 of the UN Recommendations include:

Ammonium perchlorate: classified as 1.1D (UN 0402) or 5.1 (UN 1442) with reference to its particle size, but based on test data.

Titanium (metal): has entries for dry powder UN 2546 (Div. 4.2) and sponge powders or sponge granules UN 2878 (Div. 4.1).

Titanium powder wetted: there are two particle size limits specified under the single Chapter 2 entry of UN 1352, these depend upon whether the powder is produced mechanically (53 mm) or chemically (840 mm); (see also Hafnium powder wetted UN 1326).

5. Under most circumstances testing in the form presented is appropriate e.g. classification of a metal powder should be based on the properties exhibited by the powder, not the properties of a block or granules and vice versa. A metal in the form of lumps or a coarse powder may not burn, finer powders may burn sufficiently rapidly to be classified as flammable solids, and very fine powders may be pyrophoric. However, it is not possible to predict whether or not a particular material will exhibit this range of behaviour and if so where the thresholds will occur. An educated guess can be made and may often suffice, but in practice thresholds will not be sharp. If the form of the material is changed, it may be possible to predict if the new form will behave in a similar way or if retesting is necessary, but frequently this will be limited to either minor or gross changes. Actual thresholds for changes in behaviour will need to be determined by testing, when the need arises.

6 The situation is even more complicated when classification is based on composite data (e.g. detonation, deflagration and heating under confinement). Examples where variability is observed or expected include ammonium nitrate, where density may be critical, and materials where the significant test for classification is the deflagration behaviour, when the rate of deflagration can be markedly affected by particle size.

7. A classification should therefore only apply to a substance in an appropriately defined form. This would allow materials to be classified on the basis of tests performed on "the form presented", and would ensure that classification represented, as far as is practicable, the behaviour of the material in question. It is appropriate therefore that, if testing in the form presented is adopted, the form is appropriately specified.

Special consideration of oxidising solids

8 UN test O.1: Test for oxidizing solids should be considered an exception to the principle of testing in the form presented. This is based on two factors:

(1) the definition of a solid oxidiser; and
(2) a small scale laboratory test for classification is intended to predict large scale behaviour.

9 The definition of an oxidiser refers to a substance which may assist a fire "generally by yielding oxygen" (UN Recommendations para. 2.5.1 (a)). In para 34.4.1.2.1 of the Manual of Tests and Criteria the particle size of the reference material is specified, this is so that an intimate mixture with cellulose can be obtained, and the burning rate of the mixture can be examined. The reference material is only ground if fine material (<500 mm) constitutes more than 10% of the mass of the sample or the material is friable (Test Manual 34.4.1.2.6). In practice, if a substance under the influence of heat can decompose to produce oxygen, relatively coarse material will do so in a real fire scenario. In a small scale test such as is Test O.1, even a solid the size of fertiliser prills is so coarse, relative of the size of the pile, that obtaining a suitable mixture and subjecting it to a meaningful heat challenge is almost impossible. This is certainly case for prilled ammonium nitrate fertilisers which are currently assigned UN Division 5.1, and which give negative results in small scale pile tests. A classification based on the behaviour of coarse material in a small scale test is not therefore representative of "real-life" behaviour. In the case of the oxidiser test for solids it is more appropriate to compare like with like, i.e. to test the sample in the same particle size range as that of the standard.

10. It is not always possible to grind a material prior to test, for example a waxy solid would require specialist (cryogenic) milling equipment, and under these circumstances it is reasonable to dispense with the requirement to mill. However as by far the majority of solid oxidisers are crystalline inorganic substances, this dispensation will not have a significant impact.

Proposals

11. For classification tests on solid substances (except for solid oxidisers), the tests should be performed on the substance as presented. If, for the purposes of supply or transport, the same chemical is to be presented in a different physical form which is considered likely to materially alter its performance in a classification test, the substance in the new form must be tested.

12. The technical name shall include information on the physical form of the substance, if this affects the classification.

13. If such a scheme is accepted within the GHS, then clear guidance would need to be prepared to ensure that testing was not required or demanded for every possible material form of a substance. If it is reasonably foreseeable that the material form of a substance will change significantly through its lifecycle then the potential hazards must be addressed. If the hazard is potentially increased so as to change the classification then this should be dealt with by way of calculation, inference, or in exceptional circumstances by further testing.

14. For UN test O.1 Test for Solid Oxidisers, where it is practical to grind the test substance, the test shall be performed on the substance in the same particle size range as the potassium bromate reference.

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GLOBAL HARMONISATION OF SYSTEMS OF CLASSIFICATION AND LABELLING OF CHEMICALS

Physical hazards

Organic peroxides: explosive properties

Transmitted by the European Chemical Industry Council (CEFIC)

1. Introduction

During the meetings of the joint ILO/UN-Committee Working group on Harmonised classification criteria for flammability and reactivity held in 1995/1997, the determination of the hazardous properties of organic peroxides, including explosibility, should be based on the UN manual of tests and criteria, test series A-H, see report of the working group on reactivity, document ST/SG/AC.10/23/Add.4.

This classification procedure implies that organic peroxides are classified into high and low hazardous types (organic peroxide type A to type G). Type A and type B are recognised as having explosive properties.

Based on the consensus achieved in the working group on reactivity on the testseries to be applied for organic peroxides, CEFIC proposes to assign explosive properties to organic peroxide type A and organic peroxide type B and to use an appropriate risk phrase for type C in the global harmonized system, for reasons as outlined in this proposal.

2. Justification of the proposal

In the global harmonized system, organic peroxides will be tested by the UN test series A to H. In this classification procedure, a series of tests have to be performed to determine the detonation, deflagration and thermal explosion properties. In the final assignment of an organic peroxide reacting violently in the laboratory scale tests, the execution of packaging tests is required.

In case the peroxide shows detonation or rapid deflagration in the packaging the product is forbidden for transport and classified as **type A** because of its explosive properties. In case the peroxide passes these packaging test, but based on the laboratory scale tests can detonate or deflagrate rapidly, it is classified as **type B**, and should bear an explosive label.
In case the peroxide shows violent thermal explosion in the packaging a subsidiary explosion hazard is assigned and as a consequence, the product is also classified as **type B** and should bear an explosive label.

Considering this UN classification procedure, the assignment of explosive properties (and application of explosive label) is partly based on results of tests performed with the peroxide in its commercial packaging.
In the global harmonized classification system, this way of assigning explosive properties to organic peroxides type A and type B is reasonable for transport and storage circumstances; in these two "handling phases" the product remains in its commercial package 1/.

Under a degree of confinement higher than that of the peroxide in its packaging (e.g. handling in dosing vessels, dosing lines, pumping systems, extruders etc.) some other organic peroxides may show explosive properties. This condition occurs only under processing conditions. In industry, special preventive and protective measures are issued for processing purposes. This is however not part of the global harmonization.

Nevertheless, for the products which pass the packaging tests (type C peroxides) the hazard of explosion under higher degree of confinement hazard can be communication to users of the peroxide. A risk phrase like the "**Risk of explosion if heated under confinement**" currently used in the EU regulation can be useful.

1/ *Organic peroxide storage regulations generally prescribe the use of the packaging as used for transport.*

In conclusion, CEFIC is of the opinion that the use of a hazard communication phrase in line with the current EU R44 risk phrase for organic peroxide type C and the use of this phrase together with an explosive label for organic peroxide type A and type B, is a reasonable approach for assigning explosive properties to organic peroxides and facilitates the development of a global harmonisation of classification systems.

3. Proposal

Based on the consensus reached by the working group on reactivity, the UN classification procedure will be applied for organic peroxides in the harmonised classification system (test series A-H).

In this system substances are classified into more or less hazardous organic peroxide types (organic peroxide type A to type G). As a result of this classification and based on the arguments given in section 2, CEFIC proposes the following to harmonise the assignment of explosive properties to organic peroxides:

1) *Assign to organic peroxide type A and type B:*

- explosive properties and consequent explosive labelling
- a hazard communication phrase (risk phrase) in line with current EU R44 "Risk of explosion if heated under confinement"

2) *Assign to organic peroxide type C:*

- a hazard communication phrase (risk phrase) in line with current EU R44 "Risk of explosion if heated under confinement"

A similar assignment approach of explosive properties for self-reactive substances of class 4.1 could be valid.